



INVESTOR IN PEOPLE

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Under the Companies Act does not constitute a new legal entity but merely subject to certain additional company law rules.

Signed

Dated 16 September 2004

22SEP03 E638996-1 C21729  
P01/7700 0.00-0322116.5

The Patent Office

Cardiff Road  
Newport  
South Wales  
NP10 8QQ**Request for grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



1. Your reference

SemiGap

0322116.5

2. Patent application number
- 
- (The Patent Office will fill in this part)*

Borealls Technical Limited,  
Montagu Pavilion  
8-10 Queensway  
GibraltarPatents ADP number *(If you know it)*

8565343002

If the applicant is a corporate body, give the country/state of its incorporation

Gibraltar

4. Title of the invention

Tunneling Gap Diodes

5. Name of your agent
- (If you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent  
*(including the postcode)*44 Swing Gate Lane  
BERKHAMSTED  
Hertfordshire  
HP4 2LLPatents ADP number *(If you know it)*

448448700

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and
- (If you know it)*
- the or each application number

Country

Priority application number  
*(If you know it)*Date of filing  
*(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
*(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request?
- (Answer 'Yes' or 'No')*

No

- a) any applicant named in part 3 is not an inventor, or  
 b) there is an inventor who is not named as an applicant, or  
 c) any named applicant is a corporate body.
- See note (d)*

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form

Description	7
Claim(s)	1
Abstract	1
Drawing(s)	3 only

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination  
(*Patents Form 10/77*)

Any other documents  
(please specify)

We request the grant of a patent on the basis of this application.

Signature

Date

22 September 2003

11. Name and daytime telephone number of person to contact in the United Kingdom

Dr Stuart Harbron - 01442 384084

#### Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

#### Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

## Tunneling Gap Diodes

### Field of Invention

This invention relates to tunneling diodes and their application to heat pumping and power generation.

### 5 Background of the Invention

Tunnel junctions of a new type that comprise Normal metal-Vacuum-Normal metal (NVN) have been disclosed [Avto Tavkhelidze, Larisa Koptonashvili, Zauri Berishvili, Givi Skhiladze, "Method for making diode device", US Patent No. 6,417,060 B2]. A key advantage of these junctions is the use of 10 a vacuum as the insulator. Consequently, there is formally zero heat conductivity between the electrodes, allowing the fabrication of tunnel junctions with extremely low thermal backflow.

Other groups have reported theoretical studies that seek to utilize the benefits of using a vacuum as an insulator. One group has considered 15 utilizing emission from semiconductor resonant states [A.N. Korotkov and K.K. Likharev, "Possible cooling by resonant Fowler-Nordheim emission", *Appl. Phys. Lett.* 75(16):2491-2493 (1999)]. This approach leads to a selective emission of electrons from the cathode. Another group proposes cooling via electron field emission from diamond or III-nitride thin films 20 deposited on metal or silicon substrates [P.H. Cutler, N.M. Miskovsky, N. Kumar and M.S. Chung, "New Results on Microelectronic Cooling Using the Inverse Nottingham Effect. Low temperature Operation and Efficiency", *Electrochemical Soc. Proc.* Volume 2000-28, pp 99-111 (1999)]. A yet further theoretical study has considered the how the effective work function for 25 emission may be lowered by reducing the gap between the electrodes to a nanometer, and it is predicted that a material having a work function of ~1.0eV would show an effective work function of ~0.4eV under these conditions. Experimental work using a small nm-sized gap showed the expected lowering of the vacuum barrier between the electrodes, enabling 30 emission from surfaces with work functions of ~1 eV at room temperature. [Y. Hishinuma, T.H. Geballe, B.Y. Moyzhes, T.W. Kenny, "Refrigeration by combined tunneling and thermionic emission in vacuum: Use of nanometer scale design", *Appl. Phys. Lett.* 78(17):2752-2754, (2001); Y. Hishinuma, T.H. Geballe, B.Y. Moyzhes, T.W. Kenny, "Measurements of cooling by room- 35 temperature thermionic emission across a nanometer gap", *Appl. Phys. Lett.* 94(7):4690-4696, (2003)]. Further theoretical work from this group has

suggested that the need for materials with work functions near 1.0eV (which is difficult to achieve in practice), may be circumvented by the use of a semiconductor layer on the emitter in combination with a strong electric field [Y. Hishinuma, T.H. Geballe, B.Y. Moyzhes, T.W. Kenny, "Vacuum 5 thermionic refrigeration with a semiconductor heterojunction structure", Appl. Phys. Lett. 81(22):4242-4244, (2002)].

It is well known that thermionic diodes offer the possibility of efficient cooling: every electron that leaves the emitter carries away energy  $WF + 10 2kT$  (where WF is the work function of the emitter electrode). However, for room temperature cooling effects, materials having work functions of the order of ~0.3-0.35eV are needed for the emitter, and such materials are not practically available.

For tunnel diodes having metal electrodes the situation is different. All 15 the electrons can tunnel, whether they have an energy level above the Fermi level ( $E_f$ ), or below. Those electrons which have energy E above the Fermi level, carry away energy  $E-E_f$ ; those electrons which have  $E < E_f$ , return energy  $E_f - E$  to the emitter. As a result, the sum effect is less than with 20 thermionic diodes. Common tunnel diodes with metal electrodes thus have two major drawbacks: (i) the possibility of electrons below the Fermi level tunneling; (ii) back tunneling of electrons from anode to cathode.

#### Disclosure of Invention

From the foregoing, it may be appreciated that a need has arisen for an improved tunneling gap diode in which only electrons above the Fermi level tunnel from emitter to collector, and in which back tunneling, from 25 collector to emitter, is suppressed.

The present invention discloses a tunneling diode having a band gap material as the collector. This increases the tunneling of electrons having greater energy than the Fermi level from emitter to collector, leading to an increase in the efficiency of heat pumping or power generation by the 30 diode.

The present invention also discloses a tunneling diode having a band gap material as the collector, and having a coating of the same or different band gap material on the emitter. This increases the tunneling of electrons having greater energy than Fermi level from emitter to collector, leading 35 to an increase in the efficiency of heat pumping or power generation by the diode.

For these embodiments, the band gap may be present as a layer of band gap, or may be a hetero-structured band gap layer.

The present invention also comprises a method for filtering emission from the emitter by using a collector comprised of a band gap material.

5 The present invention also comprises a method for suppressing back tunneling of electrons from collector to emitter by using a collector comprised of a band gap material.

The present invention also comprises a vacuum diode heat pump for heat pumping applications comprising the tunneling diode of the present  
10 invention.

15 The present invention also comprises an electrical power generator comprising the tunneling diode of the present invention.

#### Brief Description of Drawings

For a more complete explanation of the present invention and the technical  
15 advantages thereof, reference is now made to the following description and the accompanying drawing in which:

Figure 1 shows two embodiments of a tunnel diode device of the present invention.

20 Figure 2 shows in diagrammatic form various energy levels of a close-spaced tunnel diode of the present invention.

Figure 3 shows two embodiments of a tunnel diode device of the present invention for pumping heat or power generation.

#### Best Mode for Carrying Out the Invention

Embodiments of the present invention and their technical advantages may be better understood by referring to Figure 1A, which shows in diagrammatic form a metal emitter 102, a collector 104, an external circuit 106 and a voltage source, 108. The collector comprises a band gap material, which is to be understood in this present disclosure to indicate a material in which there is a forbidden region between a lower valence band and an upper conduction band. The band gap material may be a semiconductor, such as Ge, Si, GaAs or SiC. It also includes materials such as diamond and doped diamond. It also includes materials such as the alkaline earth oxides. Figure 1B discloses another embodiment of the present invention, in which the band gap material is deposited as a layer on a metal collector 210.

For the embodiments shown in Figure 1A and 1B, the space between the two electrodes is of the order of 1 - 20 nm, and is maintained at this distance by a housing (not shown). Preferably the space between the electrodes is evacuated, or filled with an inert gas at low pressure, such as argon.

- 5 Without wishing to be bound by a particular doctrine, the operation of the tunnel diode of the present invention may be understood by referring to Figure 1, which shows various energy levels, a metal cathode (or emitter) is positioned a small distance  $d$  away from a semiconductor cathode (or collector). Distance  $d$  is preferably of the order of 1 - 100 nm, most 10 preferably 1 - 10nm. It is well known that the Fermi level of such a semiconductor lies near the center of forbidden band  $G$ .

The vertical axis in Figure 1 represents potential energy, with zero signifying the bottom of the metal conductive band. The horizontal axis represents the distance between electrodes. Electron density in the 15 conducting band of the metal and in the conducting (upper) and valence (lower) bands of semiconductor is shown by the solid lines, and the dashed lines represent the electron states density. The difference between Fermi levels of the electrodes,  $V$ , is the applied voltage (V bias).

20  $WF_1$  is the work function of the metal,  $WF_2$  is the work function of the semiconductor, and  $G$  is the forbidden band.  $WF_2$  is the "thermionic" work function, i.e. the energy interval between the Fermi level and the vacuum function; then  $WF_{2\text{eff}} = WF_2 - G/2$  is the energy interval between the bottom of the conductive band and the electron energy level in the vacuum.

25 If the forbidden band wide  $G$  of the semiconductor is not too large (some tenth of eV), thermal excitation of electrons from the valence band into the conductive band is sufficiently fast so as not to be rate limiting, as it is shown at the figure (the electron density is the same order as in the metal at the same distances from Fermi levels). It is sufficiently for 30 electrical current transmission in semiconductor (especially if it is a layer ~10-15nm "thin" for conductivity and "thick" for tunnel processes).

From Figure 2 it can be seen that that tunnel exchange by electrons between electrodes is possible only above or below the forbidden band, because 35 forbidden band does not have any permitted electron states. Since the probability for tunneling is much less for states below the forbidden band than for states above it, tunneling from below the forbidden band can be neglected, and it is only tunneling from the conductive band that needs to be taken into account. This region has an energy level of  $G/2 - V$  above the Fermi level of emitter.

What this means is that the use of a semiconductor collector prevents tunneling from emitter to collector for electrons which lie opposite the forbidden gap of semiconductor, i.e. just below Fermi level of emitter. Moreover, the use of a semiconductor with a gap of  $E_g$  between the Fermi 5 level and the bottom of the conductive band, tunneling from emitter for electrons with energy less  $E_g$  is prevented.

A further aspect of the invention is that the application of a voltage bias  $V$  between electrodes allows electrons with energies greater than  $E_g - V$  to tunnel. In other words, the tunnel diode of the present invention is 10 equivalent to a thermionic diode with an "artificial" work function of  $E_g - V$ . The magnitude of the work function can be adjusted by the choice of  $E_g$  and  $V$ .

The semiconductor material selected is required to have a sufficiently high electrical conductivity for working currents (1-100A/cm<sup>2</sup>). 15 Referring again to Figure 2 it can be seen that electrons that tunnel will carry away from emitter energy of not less than  $G/2-V$ . As discussed above, this potential threshold ( $G/2-V$ ) is equivalent to the emitter work function in thermionic diodes, and can be adjusted to optimal low (0.2-0.3-0.4eV) value by applied voltage  $V$ . In effect this means that the tunnel diode of 20 the present invention is as efficient as a thermionic diode for cooling, and that this level of cooling can be achieved in practice without resorting to exotic materials having low work functions. In fact, its "work function" can be chosen any, and the cooling power and efficiency manipulated, varying of  $V$  and gap size  $d$ .

25 Varying the electron donor concentration allows the position of the Fermi level to be moved from the centre of the forbidden gap to nearer the bottom of the conductive band. This means that a range of semiconductors may be used, including Ge ( $G=0.75\text{eV}$ ), Si ( $G=1.12\text{eV}$ ), GaAs ( $G=1.43$ ) or SiC ( $G=2.4-3.4\text{eV}$ ), and the effective work function be modified to nearer 0.3-0.4eV by 30 appropriate doping, or by utilizing a hetero-structure semiconductor.

Even for semiconductors with high doping by electron donor dopant (such semiconductors has minimum  $E_g$ )  $E_g$  is not less 0.05-0.1eV. So, in principle, all semiconductors with low  $E_g$  can give positive effects and are suitable.

For semiconductors with a large  $E_g$  (for example,  $E_g>1\text{eV}$ ), the tunnel current 35 from the emitter will be too small at low  $V_{bias}$  values of ~0.1 - 0.2V. However at  $V_{bias}$  values of 0.3 - 0.4V, the effective barrier will be optimum for room temperature cooling (0.3 - 0.4eV). In other words, adjusting the bias level so that  $E_g - V_{bias} = 0.3-0.35\text{eV}$  corresponds to

optimum emitter WF of thermionic cool diode for chosen emitter and collector temperatures). Even if  $E_0$  is in the range 3-4eV, V bias can be set at 2.7 - 3.7V. Of course, such high biases values will give lower efficiency, but reasonable currents can be obtained at  $d = \sim 50\text{nm}$ , compared to  $d = \sim 2\text{nm}$  for  $\sim 10\text{A/cm}^2$  currents and a  $V_{bias} \sim 0.1\text{V}$  for high efficiency cooling operation.

Thus there is a wide range of semiconductor materials that may be used as the band gap material in the tunnel gap diode of the present invention for cooling applications. The two key design features are that (i) the band gap material used must have sufficient conductivity; and (ii) the band gap material should give low WF ( $\sim 1 - 1.2\text{ eV}$ ) after  $\text{Cs} + \text{O}_2$  treatment (or by treatment of another electropositive atoms such as another alkali metals, alkali-earth metals (Ba, Sr), La, Y, Sc etc., and other electronegative atoms (F and another halogens, S, etc)).

For power generating applications the output voltage is small ( $\sim 0.1\text{V}$  or less), and so  $E_0$  should be less  $\sim 0.2 - 0.4\text{eV}$  for emitter temperatures 300-400K. But for higher temperatures (500 - 600 - 700K) the preferred value for  $E_0$  rises, and for 700-800K it can be  $\sim 1\text{eV}$ .

#### Example

In one embodiment, pure Ge is the semiconductor. It has  $G = 0.7\text{eV}$ , and  $G/2 = 0.375\text{eV}$ , a little more than optimum WF for thermionic diode for  $T_c = 300\text{K}$  ( $\sim 0.33\text{eV}$ ). Even at room temperature Ge has electron concentration in conductive band  $\sim 10^{13}\text{ cm}^{-3}$  - it is sufficiently for electrical conductivity for thin layer. If we assume, that electrode are treated by  $\text{Cs}$  and  $\text{O}_2$  and has  $\text{WF1}=\text{WF2}=1\text{eV}$  (our standard), we have next output parameters for Cool Chips with  $d = 2.5\text{nm}$ ,  $T_c=300\text{K}$ ,  $T_h=350\text{K}$ :

$V, \text{V}$	$j, \text{A/cm}^2$	$Q_c, \text{W/cm}^2$	$W, \text{W/cm}^2$	COP	$h_{cool}$	$h_{cool}/h_{cool}$ Carnot
0.10	1.76	0.63	0.177	3.56	0.78	0.91
0.14	6.82	2.22	0.796	2.32	0.699	0.816
0.20	36.6	9.70	7.315	1.32	0.57	0.665

Here  $j$  is resulting diode current,  $Q_c$  cooling power,  $W = j*V =$  spent power. Calculations were fulfilled according to "new" model with some simplifications, which can decrease (not increase!) results. As you see, for low biases we have very high efficiency, but relatively low cool power.

But at a little increase of V the cool power risen up more than on the order (to ~10W/cm<sup>2</sup>), and efficiency drops not too much (COP>1).

Note, by a bit decreasing of the gap (to 2nm) we can significantly improved output parameters:

V, V	j, A/cm <sup>2</sup>	Qc, W/cm <sup>2</sup>	W, W/cm <sup>2</sup>	COP	hcool	hcool/hcool Carnot
0.1	44.6	15.6	4.46	3.57	0.78	0.908

- 5 It is very important, for these conditions it is possible to have a good parameters even for WF>1eV at more thin gaps. For example, for WF = 1.3eV (it is common value for anodes of common thermionic converters!) by decreasing of the gap to d=1.6nm we can have:

V, V	j, A/cm <sup>2</sup>	Qc, W/cm <sup>2</sup>	W, W/cm <sup>2</sup>	COP	hcool	hcool/hcool Carnot
0.12	19.3	6.13	2.32	2.646	0.726	0.847

- 10 Of course, it is possible to use another semiconductor materials, which can give still better parameter, including special one for tunnel chips (now to create the material with special properties isn't a problem). Of course, for different cooling tasks it needs difference materials. Also, use of semiconductor collector is favorable for power producing too. For this purpose special materials are optimal.

- 15 Referring now to Figure 3, which shows in diagrammatic form a heat pump / power converter of the present invention comprising an emitter, a collector and a bias circuit. In Figure 3A, the collector is a semiconductor material. In Figure 3B, the collector is a layer of a semi conductor material on a metal electrode. The tunnel gap diode is additionally connected via an external circuit 302 to a power supply (for heat pumping applications) or an electrical load (for power generating applications). For power generating applications, the voltage bias source 208 and corresponding circuit 206 is not required.

Claims

1. A tunnel diode in which the collector comprises a band gap material.
  2. The tunnel diode of claim 1 additionally comprising an emitter coated with a layer of a band gap material material.
  - 5 3. The tunnel diode of claim 1 or claim 2 in which the collector comprises a layer of band gap material deposited on a metal collector.
  4. The tunnel diode of any of the preceding claims in which the band gap material is a semiconductor.
  - 10 5. The tunnel diode of any of the preceding claims in which the electrodes are separated by a gap in the range 1 - 50 nm.
  6. The tunnel diode of claims 4 or 5 in which a gap between the emitter and collector electrodes is evacuated.
  7. A vacuum diode heat pump comprising the tunnel diode of any of the preceding claims.
- 
- 15 8. A thermionic converter comprising the tunnel diode of claims 1 to 6.
  9. A method for preventing back tunneling of electrons in a tunnel diode comprising the step of coating the collector with a layer of a band gap material.
  - 20 10. The method for preventing back tunneling of electrons of claim 9 in which the band gap material is a semiconductor.
  11. A method for promoting the tunneling of electrons having an energy level higher than the Fermi level from an emitter surface, comprising the step of providing a collector comprising a band gap material.
  - 25 12. The method for preventing back tunneling of electrons of claim 11 in which the band gap material is a semiconductor.

ABSTRACT

The present invention discloses a tunneling diode having a band gap material as the collector. This increases the tunneling of electrons having greater energy than the Fermi level from emitter to collector, leading to  
5 an increase in the efficiency of heat pumping or power generation by the diode. This approach also reduces back tunneling of electrons from collector to emitter.

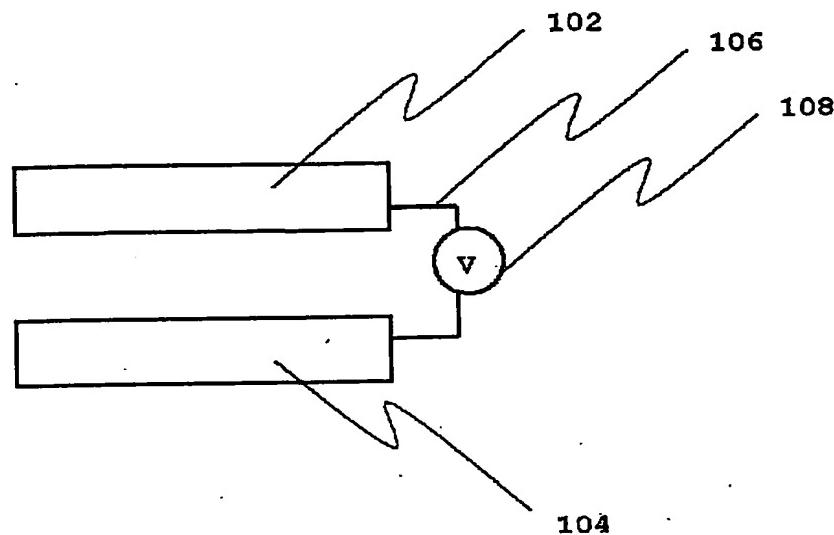
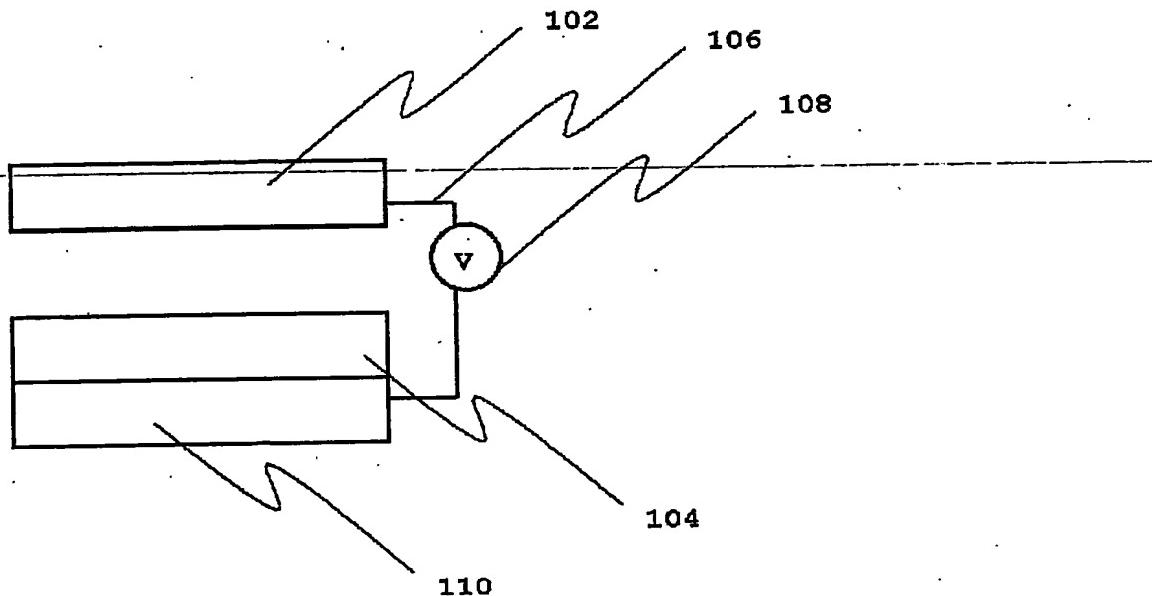
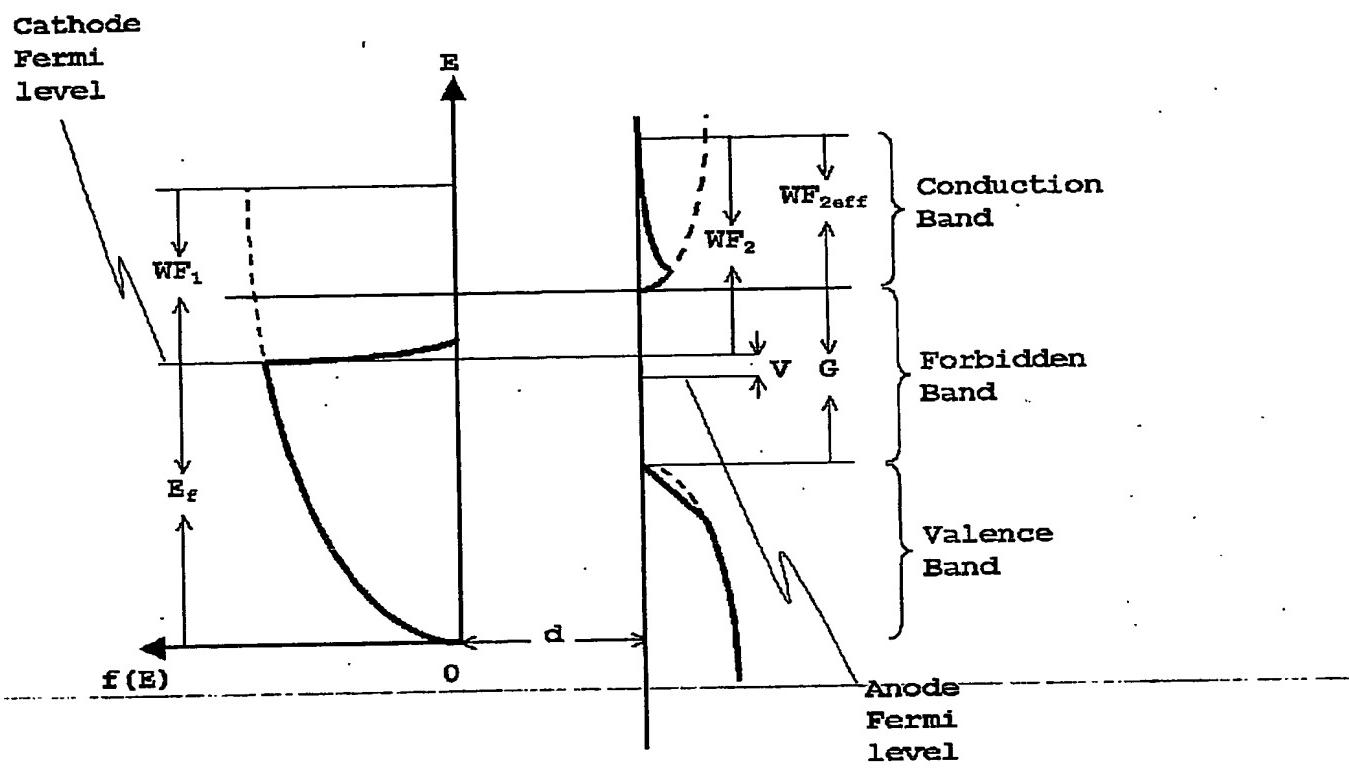
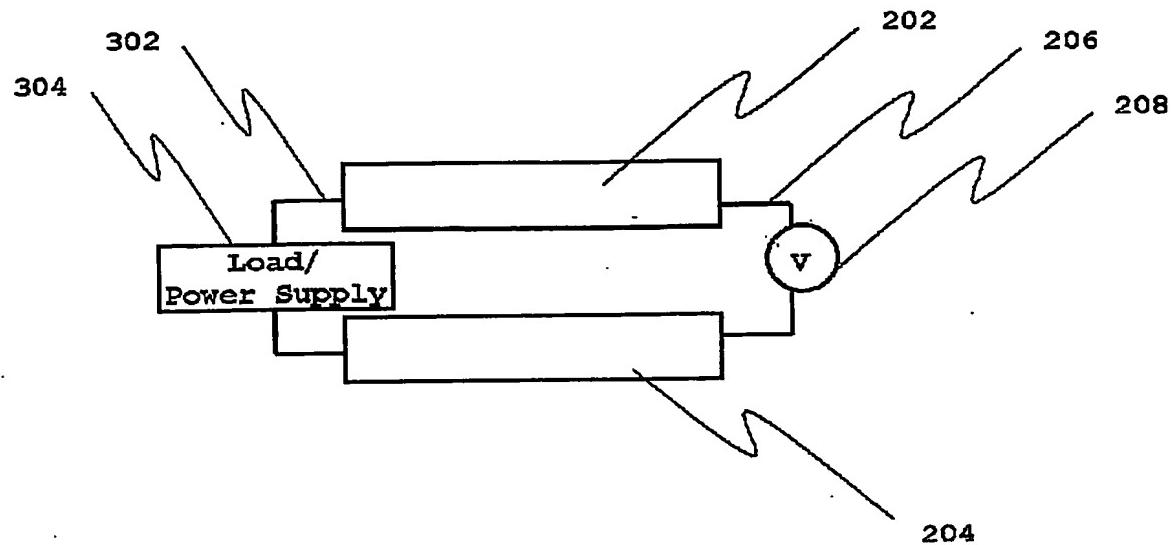
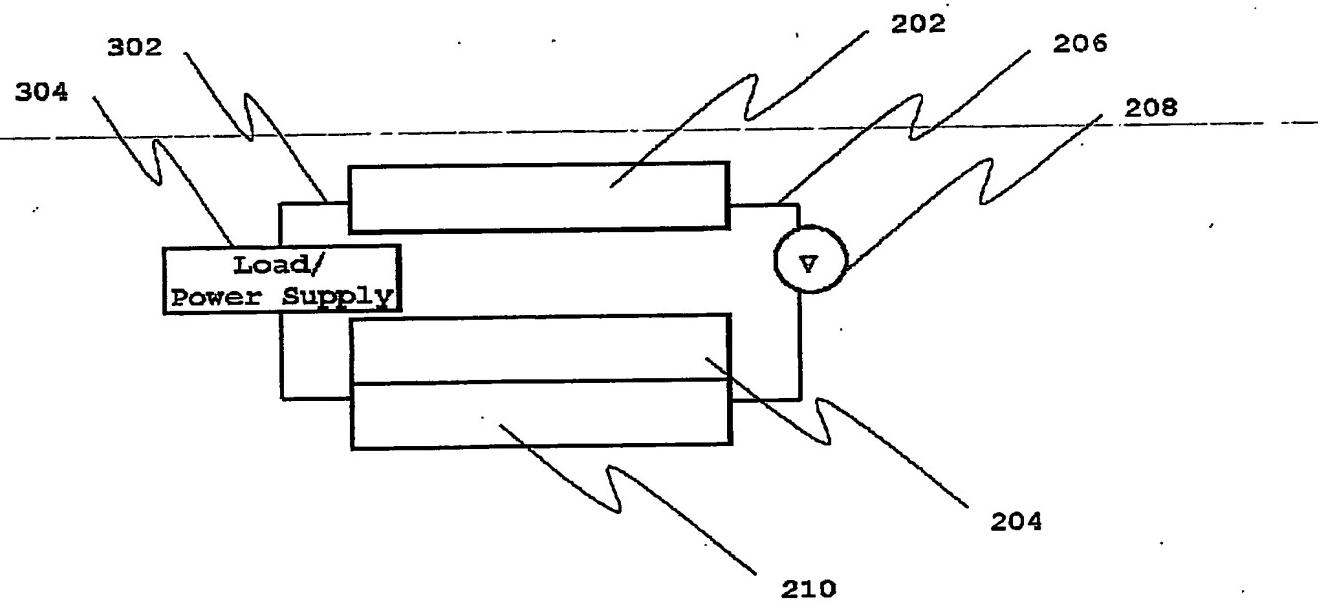
Figure 1AFigure 1B

Figure 2

— Electron density

- - - Electron states density

Figure 3AFigure 3B

# **Document made available under the Patent Cooperation Treaty (PCT)**

International application number: PCT/US04/031221

International filing date: 22 September 2004 (22.09.2004)

Document type: Certified copy of priority document

Document details: Country/Office: GB  
Number: 0322116.5  
Filing date: 22 September 2003 (22.09.2003)

Date of receipt at the International Bureau: 21 November 2005 (21.11.2005)

Remark: Priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**